Process studies of the air-sea exchange of carbon dioxide in the Atlantic Ocean

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SUMMARY

Oceanic uptake of CO_2

The burning of fossil fuel burning as well as the manufacturing of cement release large amounts of the greenhouse gas carbon dioxide (CO_2) into the atmosphere. Concern about the increasing atmospheric CO_2-content (Keeling *et al.*, 1989) and its expected consequence of global warming (Arrhenius, 1896; Houghton *et al.*, 1996) have promoted research on the atmospheric budget of CO_2. The oceans are estimated to absorb roughly 33 percent or 2.0 ± 0.8 Gt C yr^{-1} (1 Gt C or 10^{15} g C) of the CO_2 emitted by anthropogenic activity (Schimel *et al.*, 1995). The atmospheric CO_2-content consistently displayed a minimum at about 30°-50°S in the years between 1962 and 1986 (Keeling *et al.*, 1984, 1989). As the oceans cover most of the globe at these latitudes, the atmospheric CO_2-minimum suggests an important oceanic sink within this latitudinal band (Chapter 1).

This thesis attempts to answer some of the questions with regards to the oceans as a blue black box in the global carbon cycle and to the exchange of CO_2 between the oceans and the atmosphere. Surface-water CO_2-measurements have been made during five cruises on R.V. *Polarstern* to verify the working hypothesis of oceanic CO_2-uptake at 30°-50°S in the Atlantic Ocean (Chapter 5, 6). The physical and biological processes influencing the dissolved inorganic carbon system in surface-water and the air-sea exchange of CO_2 have been investigated for Dutch coastal waters (Chapter 8), the Atlantic Ocean and the Atlantic sector of the Southern Ocean (Chapter 5-7).

Air-sea exchange of CO_2

Fundamental questions still prevail on the nature of the air-sea exchange of CO_2 at the highly dynamical sea surface (Liss and Slater, 1974; Liss, 1983; Thorpe, 1984, 1995; Liss and Merlivat, 1986; Wanninkhof, 1992; Woolf, 1993, 1995; Liss *et al.*, 1997) (Chapter 3, 9). The air-sea exchange of CO_2 (F_{dd}) is generally described as the product of a gas transfer velocity k_w and the difference of the CO_2-concentration between bulk water $[CO_{2T}]_{bulk}$ and marine air $[CO_{2T}]_{air}$ (Liss and Merlivat, 1986) (Chapter 3):

$$F_{dd} = k_w ([CO_{2T}]_{bulk} - K'_0 fCO_{2air}) \quad (3\text{-}8)$$

$$[CO_{2T}] = K'_0 fCO_2 \quad (2\text{-}20)$$

The temperature and salinity dependent solubility K'_0 relates the concentration of dissolved CO_2 [CO_{2T}] to its fugacity (fCO_2) in an overlying gas volume (Chapter 2, 3). A temperature gradient at the sea surface, the skin effect, influences the exchange (Robinson *et al.*, 1984; Robertson and Watson, 1992; Van Scoy *et al.*, 1995) (Chapter 3). The kinetics of the exchange are a function of surface turbulence (Jähne *et al.*, 1987) and the density of bubbles (Woolf, 1993), both depending on wind speed, sea state and the presence of surfactants, mainly organic surface films.

The atmospheric CO_2-content is relatively constant over large horizontal distances. In contrast, the concentration of dissolved CO_2 $[CO_{2T}]_{bulk}$ is highly variable in oceanic surface-waters in response to temperature and salinity changes, mixing and biological activity. The spatial and temporal variability of the air-sea exchange of CO_2 (F_{dd}) largely depends on the distribution of wind speed, the concentration of dissolved CO_2 and the solubility K'_0. Dissolved CO_2 constitutes roughly 1 percent of total dissolved inorganic carbon (DIC or TCO_2) in seawater. DIC varies by biological activity and conservative mixing (Chapter 2).

Changes of fCO_2 and a budget of DIC during spring in the Southern Ocean

A time series in austral spring 1992 has demonstrated differences in the relative importance of biological and physical processes for surface-water fCO_2 in the Polar Frontal region and in the open waters of the Antarctic Circumpolar Current (ACC) at 6°W (Chapter 5). In the Polar Frontal region from 47° to 50°S the fCO_2 decreased from slightly below the atmospheric value to 50 µatm below it. Photosynthetic uptake of CO_2 by developing diatom blooms was responsible for this decrease of fCO_2. Seasonal warming of 1.2°C and air-sea exchange of CO_2 partly compensated the decrease of fCO_2. A budget of DIC in the mixed layer showed that the proportion of the decomposition of organic matter to net primary production increased from 5 to 47 percent during the development of the spring bloom. The apparent carbon export was 21 percent of the net primary production. Vertical advection, diffusion and air-sea exchange of CO_2 were small terms in the budget of DIC for the Polar Frontal region (Chapter 5).

From 50° to 56°S, in the southern part of the ACC and the southern Frontal region, fCO_2 increased 7-8 µatm as a result of surface-water warming of 0.5°C. DIC-changes in the mixed layer were small, suggesting that the observed low net primary production was compensated to a large extent by the decomposition of organic matter. At 56°S, south of the southern Frontal jet, a sharp rise of fCO_2 occurred. The ACC-Weddell Gyre Boundary and the Weddell Gyre from 56° to 60°S were strong oceanic sources of CO_2 after the retreat of the ice (Chapter 5).

The relationship between fCO_2 and the chlorophyll *a* content changed with time from 47° to 60°S. The region of 47° to 60°S at 6°W was a slight oceanic sink of CO_2 in austral spring 1992. The size of the estimated uptake depended on the

parameterization of the gas transfer velocity and the assumption of a temperature gradient at the sea surface (Chapter 5).

Controls on the air-sea flux of CO_2 for the Atlantic Ocean

One of the main results of this thesis is the observation of the key role of ocean circulation in the distribution of surface-water CO_2-characteristics. Reccurring latitudinal patterns with strong gradients at hydrographic fronts have been observed for fCO_2 and DIC in surface-waters of the Atlantic Ocean and of the Atlantic sector of the Southern Ocean (Chapter 5-7). Ocean circulation leaves its imprint on the CO_2-chemistry of these surface-waters. Warming and cooling along the boundary currents of the subtropical gyres, high rainfall in the Intertropical Convergence Zone (ITCZ), coastal and equatorial upwelling and the ensuing elevated biological activity all affect the basin-wide distribution of surface-water fCO_2 and DIC (Chapter 5-7).

Surface-water fCO_2 and the air-sea exchange of CO_2 in the Atlantic Ocean have an asymmetrical distribution across the equator as a result of equatorial upwelling, warming op the upwelled water, dilution by high rainfall in the ITCZ and net northward heat transport from the southern to the northern hemisphere (Chapter 6). Oceanic release of CO_2 occurs mainly in the southern subtropical gyre, while uptake dominated in the northern gyre. The observed strong oceanic uptake of 0.2 Gt C yr^{-1} for 40°-55°S in the South Atlantic Ocean (Chapter 6) along with recent estimates for the other oceans (Takahashi, 1989; Murphy *et al.*, 1991a; Louanchi *et al.*, 1996) corroborate the hypothesis of oceanic uptake of CO_2 at southern latitudes as suggested by the minimum of the atmospheric CO_2-content for 30°-50°S (Chapter 6). The larger surface-area of sinks than of sources make the Atlantic Ocean from 45°N to 55°S, a net sink of atmospheric CO_2 of 0.5-0.7 Gt C yr^{-1} (Chapter 6).

The dependence on temperature and salinity of DIC

Calculated titration alkalinity (TA) has an almost linear relationship with salinity. Changes of DIC depend both on temperature and salinity (Chapter 7). The latitudinal distribution of DIC in East Atlantic surface-waters has been inferred with an accuracy of 17 μmol kg^{-1} and a standard deviation of 13 μmol kg^{-1} from *in situ* temperature, salinity and fCO_2 and values for TA and nutrient contents normalized to *in situ* salinity (scenario D) (Chapter 7).

Dissolved carbon dioxide in Dutch coastal waters

The role of shelf seas in the global carbon cycling is poorly understood (Hoppema, 1991b; Kempe and Pegler, 1991; Frankignoulle *et al.*, 1996a, b; Chapter 8). The carbonate system in Dutch coastal waters has been observed to be highly variable in September 1993. This variability has been related to changes in tidal mixing, wind speed, wind direction, coastal upwelling, river input and biological processes (Chapter 8).

The oceans: a blue black box

The past decade many new insights have been obtained in the processes controlling the uptake of atmospheric CO_2 by the oceans. A better knowledge has been achieved of the spatial and temporal distribution of surface-water fCO_2 and of the air-sea exchange of CO_2 (Murphy *et al.*, 1991a, b; Inoue *et al.*, 1992, 1995; Poisson *et al.*, 1993; Takahashi *et al.*, 1993; Feely *et al.*, 1995; Wanninkhof *et al.*, 1996; Chapter 5-8). The understanding of oceanic carbon cycling (Chipman *et al.*, 1993; Robertson *et al.*, 1993; Bates *et al.*, 1996; Chapter 5) and of the relative changes of carbon to nutrients (Redfield ratios) (De Baar *et al.*, 1997) has considerably advanced in recent years. The effects on biological activity of grazing, of the availability of light, of CO_2 (Riebesell *et al.*, 1993) and of major and trace nutrients (De Baar *et al.*, 1995; Coale *et al.*, 1996) are presently highly debated (Chapter 9).

Traditionally the CO_2-exchange between atmosphere and oceans has largely been ascribed to physical rather than biological processes. However, recent investigations have shown that biological driven exchange is in fact very important (Bates *et al.*, 1996; Cooper *et al.*, 1996; Stoll *et al.*, 1996a, b; Chapter 5). The oceanic uptake of CO_2 has generally been attributed to an increased physical carbon pump, while changes of the biological pump by increased atmospheric CO_2-levels have been deemed unlikely (Jahnke, 1990; Sarmiento and Siegenthaler, 1992). Lately, it has been stressed that enhanced CO_2-levels may well stimulate algal growth and change Redfield ratios, which would affect the biological pump (Riebesell *et al.*, 1993, 1997) (Chapter 9).

Future research programs should provide global distributions of surface-water fCO_2 and of the air-sea exchange of CO_2, which are better balanced in space and time (Chapter 9). Priority should be given to construct carbon budgets, time series and sampling networks for strategic regions, in order to obtain a better insight in oceanic carbon cycling. One strategic region should be the Southern Ocean, with emphasis on the seasonal ice zone, and the frontal band between the Subtropical Front and the Polar Front. Other strategic regions should be the Equatorial Pacific Ocean, the northern North Atlantic Ocean and coastal seas.

The deployment of autonomous drifting or moored buoys (Merlivat and Brault, 1995; Merlivat, 1997; Bakker *et al.*, 1997, submitted) can extend the coverage of surface-water fCO_2-measurements. The continuing availability and the increasing use of satellite observations is highly important for oceanic CO_2-research (Chapter 9). Notably the new SEAWIFS observations of ocean colour now provide the spatial and temporal distribution of algal blooms, which are driving the biological uptake of CO_2 by the oceans. Our emerging understanding of the oceans, the oceanographers' blue black box, will continue to raise fundamental questions on the cycling of carbon and other elements, on the control of the biological activity and on the complex interactions between the oceans and climate (Chapter 9).

This thesis has revealed the important role of oceanic circulation in determining the distribution of surface-water fCO_2 and of the air-sea flux of CO_2 (Chapter 5, 6). A six-weeks time series between 47° and 60°S at 6°W has unravelled the inorganic carbon budget of the mixed layer in one region with both developing diatom blooms and seasonal warming and in an adjacent region with 'only' seasonal warming (Chapter 5). The South Atlantic Ocean is an important sink for atmospheric CO_2 for 40° to 55°S (Chapter 6), which confirms the original hypothesis of the project.